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(54) **Method of making a CO_2 sensor**

(57) A method of making a CO_2 sensor, which has an electrochemical cell applied to a substrate in thick-film technology, is described. $NaHCO_3$, $KHCO_3$ and/or $LiHCO_3$, which upon sintering are converted to Na_2CO_3, K_2CO_3 and/or Li_2CO_3, are used as starting materials for the sensitive coating of the work electrode of the sensor. Reproducible properties of the sensitive coating of the work electrode are obtained in this way.

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The invention relates to a method of making a CO_2 sensor, which has an electrochemical cell with solid-state ion conductors applied to a substrate in thick-film technology, with a work electrode, a solid electrolyte and a counter-electrode, where the components applied to the substrate are heated for the purpose of sintering the ceramic components.

Concerning the related art, reference is also made to an article of Maruyama and co-workers, which appeared in Solid State Ionics 23 (1997), pages 107 to 112. A CO_2 sensor that consists of solid-state ion conductors, where Na_2CO_3, Nasicon and gold paste in tablet form are used, is described there.

However, it has been found that, for the work electrode, Na_2CO_3, K_2CO_3 or Li_2CO_3 cannot be printed directly in thick-film technology, because these substances are hygroscopic. In making the suspension for printing, the rheological properties of the paste or suspension would therefore not be reproducible, because their viscosity may be altered.

Starting out from a method having the features mentioned at the beginning, the object of the invention therefore is to conduct it in such a way that the sensitive coating of the work electrode is made with reproducible properties.

To accomplish this object, the invention is characterized in that for the work electrode Pt and/or Au are printed and provided with a sensitive coating, for which a suspension of $NaHCO_3$, $KHCO_3$ and/or $LiHCO_3$ is used as starting material, which starting material is converted upon heating to Na_2CO_3, K_2CO_3 and/or Li_2CO_3.

Thus, the materials indicated, which are not hygroscopic and which therefore can be made with exactly reproducible properties, are used as starting material for the sensitive coating of the work electrode. Upon heating, these are converted to the said end products desired in each instance, while simultaneously produced products of conversion are vaporized.

The stability of the sensitive coating of the work electrode is further increased when, before baking, MCO_3 or A_2CO_3 is admixed in parts of up to 10 mol%, preferably

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in parts of 1 to 8 mol%, with M = Sr or Ba and A = LI or K, with the starting suspension for the work electrode. At the same time, this admixture increases the electrical conductivity of the substances concerned.

An important embodiment of the invention is characterized in that for the work electrode Pt or Au is printed in line form, preferably serpentine-shaped or comb-shaped, in such a way that as great as possible an area of contact between the three phases, Pt or Au, the sensitive coating and the solid electrolyte, is obtained. Namely, the sensitivity of the sensor at this spot is dependent upon the three phases making contact here (Pt or Au, the sensitive coating and the solid electrolyte) and owing to the aforementioned line shape of Pt or Au the contact areas of the three phases are correspondingly and perceptibly increased.

With regard to conversion of the starting products to the end products upon heating, the following is stated:

Upon heating, $2NaHCO_3$ decomposes at over 65°C into CO_2, H_2O and Na_2CO_3. Above about 300°C, conversion is complete.

$2KHCO_3$ decomposes upon heating to about 200°C into K_2CO_3, H_2O and CO_2.

$LiHCO_3$ is stable up to about 30°C. $2LiHCO_3$ decomposes upon further heating into Li_2CO_3 and H_2O and CO_2.

Accordingly, upon heating, the particular end product desired in each instance is obtained, specifically together with water vapor and CO_2, which escape in the form of gas.

In making the sensor, a heating layer preferably is simultaneously printed on a substrate bearing the sensor components - specifically, preferably on the underside of the substrate because there is room there - which provides for the necessary operating temperature of the sensor. These measures are known per se in outline from the journal "Battelle-Information."

Claims 4 to 8 characterize preferred embodiments of a sensor made by the method according to the invention.

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At the same time, Claim 4 indicates the basic composition of the solid electrolyte, dependent upon the composition of the work electrode selected in each instance. The structure according to one of the possibilities indicated in Claim 4 is retained in all embodiments.

Claims 5 to 8 characterize variants of the composition of the counter-electrode of the sensor, where, with the embodiment according to Claim 8, O_2 can in addition be measured.

In the following, the invention is explained in detail by way of examples, in which additional important features appear. In the drawing,

Figs. 1 - 4 show, schematically, four embodiments of CO_2 sensors according to the invention, in a partially sectioned side view in each in- stance and

Figs. 5 and 6, a top view of the sensors for representation of the comb shape (Fig. 5) and the serpentine shape (Fig. 6) of the Pt and Au part of the work electrode of the sensors.

For simplification, in Figs. 1 - 4 for the work electrode only Pt and Au (porous) with a coating of Na_2CO_3 have been shown and for the solid electrolyte only Nasicon has been indicated in each instance. In this connection, however, all combinations according to Claim 4 are possible.

With regard to the counter-electrode, in the example of Fig. 2, all combinations of Claim 5 are possible.

In Figs. 1, 3 and 4, the possible combinations of the counter-electrode possible in each instance have been indicated in these figures.

For illustration, the structure of the electrochemical cell concerned in each instance has been indicated under Figs. 1 - 4 according to the example of the figure concerned, the phase limits being separated from one another by vertical lines.

In Figs. 1 and 3, it appears that effectively only the partial pressure of CO_2 is measured.

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In Fig. 2 a cell voltage is measured that indicates the concentration of CO_2 and O_2 together.

In Fig. 4 the concentration of CO_2 and, in addition and independently thereof, that of O_2 is measured.

Figs. 5 and 6 show the comb shape (Fig. 5) of Pt or Au as part of the work electrode and its serpentine shape (Fig. 6). These line shapes act to enlarge the contact surfaces between the three phases, Pt or Au, the sensitive coating, for example Na_2CO_3, and the solid electrolyte, for example Nasicon.

The operating temperature of the sensor that is heated by the heating layer is between about 100 and 600°C, depending upon the embodiment.

The sensor is made in thick-film technology, i.e., in screen printing technology, with subsequent heating of the applied layers for the purpose of sintering the ceramic.

Claims

1. Method of making a CO_2 sensor, which has an electrochemical cell with solid-state ion conductors, applied to a substrate in thick-film technology, with a work electrode, a solid electrolyte and a counter-electrode, where the components applied to the substrate are heated for the purpose of sintering the ceramic components,

   characterized in

   that for the work electrode Pt and/or Au are printed and provided with a sensitive coating, for which a suspension of $NaHCO_3$, $KHCO_3$ and/or $LiHCO_3$ is used, which starting material is converted upon heating to Na_2CO_3, K_2CO_3 and Li_2CO_3.

2. Method according to Claim 1,
characterized in
that, before baking, MCO_3 or $A2CO_3$ and/or powder, which consists of the solid electrolyte, is admixed in parts of up to 10 mol%, preferably in parts of 1 to 8 mol%, with M = Sr or Ba and A = Li or K, with the starting suspension for the work electrode..

3. Method according to Claim 1 or 2,
characterized in
that for the work electrode Pt or Au is printed in line form in such a way that as great as possible an area of contact between the three phases, Pt or Au, the sensitive coating and the solid electrolyte, is obtained.

4. CO_2 sensor, made by the method according to any of Claims 1 to 3,
characterized in
that its solid electrolyte consists of Nasicon, Na-β-Al_2O_3 or Titsikon when its work electrode contains Na_2CO_3, or consists of khibinskite, wadeite or K-β-Al_2O_3 when its work electrode contains K_2CO_3, or consists of Li-β-Al_2O_3 or $LiAlF_6$ when its work electrode contains Li_2CO_3.

5. CO_2 sensor according to Claim 4,
characterized in
that its counter-electrode consists of Na_xWO_3, K_xWO_3 or Li_xWO_3 when its work electrode contains Na_2CO_3, K_2CO_3 or Li_2CO_3.

6. CO_2 sensor according to Claim 4,
characterized in
that its counter-electrode consists of Pt and/or Au.

7. CO_2 sensor according to Claim 4,
characterized in
that its counter-electrode consists of ZrO_2 with a coating of Pt and/or Au.

8. CO_2 sensor according to Claim 4,
characterized in
that its counter-electrode consists of Pt and/or Au with a middle coating of ZrO_2 and with an upper coating of Pt and/or Au.

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Fig. 1:

Anschlussleiter = connecting conductor

Pt oder Au = Pt or Au

Substrat = substrate

Heizschicht = heating layer

Arbeitselektrode = work electrode

Festelektrolyt = solid electrolyte

Gegenelektrode = counter-electrode

Fig. 2:

Einkapselung = encapsulation

Natriumwolframbronze = sodium wolfram bronze

Pt oder Au = Pt or Au

Substrat = substrate

Heizschicht = heating layer

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Fig. 3:

Substrat = substrate

Heizschicht = heating layer

Fig. 4:

Substrat = substrate

Heizschicht = heating layer

EMK = EMF
Messung von O_2 = measurement of O_2

EMK = EMF
Messung von CO_2 = measurement of CO_2

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Fig. 5

Anschlussleiter = connecting conductor

Substrat = substrate

Fig. 6:

Anschlussleiter = connecting conductor

Substrat = substrate

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EUROPEAN SEARCH REPORT

RELEVANT DOCUMENTS

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to Claim Nos.	Classification of application (Intl. Cl.5)
A, D	SOLID STATE IONICS Vol. 23, 1987, pp. 107-112, Amsterdam, NL; T. MARUYAMA et al.,: "Potentiometric gas sensor for carbon dioxide using solid electrolytes" * Entire publication *	1	G 01 N 27/407
A	EP-A-0 182 921 (KABUSHIKI KAISYA ADVANCE KAIHATSU KENKYUJO) * Abstract; page 3, line 34 *	1	
A	SOLID STATE IONICS Vol. 24, No. 4, September 1987, pp. 281-287, Amsterdam, NL; T. MARUYAMA et al.: "Electromotive force of a CO-CO2 sensor in CO-CO2-H2-H2O atmospheres and simultaneous determination of partial pressures of CO and CO2" * Entire publication *	1	

Subject areas searched (Intl. Cl.5)

G 01 N

The present search report has been prepared for all patent claims

Place of search	Date search completed	Examiner
Berlin	30 October 91	BRISON O.P.

CATEGORY OF DOCUMENTS CITED

A Technologic background
D Document mentioned in application

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